# SYNTHETIC ORGANIC CHEMICALS

Surface-active Compounds

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SURFACE-ACTIVE COMPOUNDS comprise a new group of organic chemicals just as do the vitamins, hormones, and dyes. They may be defined broadly as organic compounds that have molecular weights of about 200–1000 and that contain at least one water-soluble group. Thus, they tend to collect at, and modify, interfaces.

All surface-active compounds are to some degree detergents, wetting agents, and emulsifying agents. The classes overlap, but, in general, the best detergents contain a long hydrocarbon chain of 16–18 carbon atoms, with a water-soluble group located at one end of the chain; while the best wetting and penetrating agents contain their water-soluble group nearer the center of the molecule. For example, sodium stearyl-sulfonate (1) is a good detergent but an inferior wetting agent compared to sodium dioctyl sulfosuccinate (2).

(1) $CH_3(CH_2)_{17}SO_2ONa$

(2) $C_8H_{17}OOC \cdot CH_2CH \cdot COOC_8H_{17}$
$$\underset{SO_2ONa}{\overset{|}{}}$$
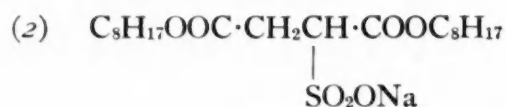
In the experience of the author, no broad structural relationship can be used to typify emulsifying agents.

The oldest and best-known surface-active compounds are the soaps—the alkali salts of the fatty acids; and these have by no means been replaced by the large number of new materials. Soaps, aided by sodium silicates, sodium hexametaphosphate, sodium and potassium pyrophosphate, and sodium carbonate, are still preferred for laundry and general detergent use. For many purposes, however, soaps have disadvantages: they cannot be used effectively in hard water or in acids; some become rancid; the lime soaps deposit in fibers and prevent level dyeing; and residual quantities leave fibers grey rather than white.

The disadvantages of soaps led to the early use of sulfonated oils in the dyeing industry; as early as 1790, mixtures of fat and sulfuric acid were employed. Runge, in 1834, prepared sulfonated oleic acid, and this was utilized until 1875, when sulfonated castor oil (Turkey Red Oil), which is still popular, was introduced. The main active ingredient in the latter is probably a sulfated ricinoleic acid salt—

(3) $CH_3(CH_2)_5 \cdot CH \cdot CH_2 \cdot CH = CH(CH_2)_7 -$
$$\underset{OSO_2ONa}{\overset{|}{}} \qquad COONa$$
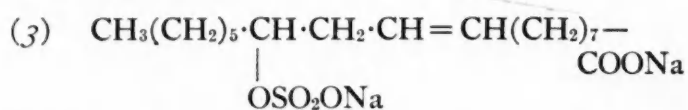
Although sulfonated oils are poor detergents, they are valuable reagents in textile processing because they are fairly good wetting agents for fabrics, are neutral and stable to acids, and are not precipitated by hard water.

In 1898, Twitchell improved the method of hydrolyzing fats to glycerol

and fatty acids by the use of catalysts (4)—emulsifiers—made from naphthalene, oleic acid, and sulfuric acid.

(4) $CH_3 \cdot (CH_2)_7 \cdot CH \cdot CH_2 \cdot (CH_2)_7 \cdot COOH$

$-SO_2OH$
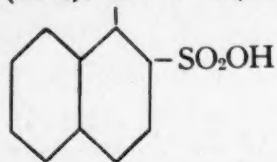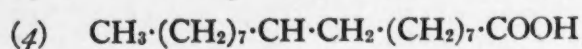
The Twitchell process was employed and studied extensively in Germany, and was probably the basis for the development of many synthetic wetting agents of this type. Twitchell also made sulfoöleic acid for the same purpose.

In 1916, Reychler prepared and studied cetyl sulfonic acid and its salts. In the years that followed, mineral oil sulfonates were patented (1919), as well as sodium tetralin sulfonate and octahydroanthracene sulfonate (1923). Directly related to the Twitchell reagents are the butylated and multipropylated aromatic sulfonates (1925-1930). Perhaps the best wetting agent of this group is sodium triisopropyl naphthalene sulfonate—

(5) $(CH_3)_2CH$ $-SO_2ONa$ $-CH(CH_3)_2$ $CH(CH_3)_2$
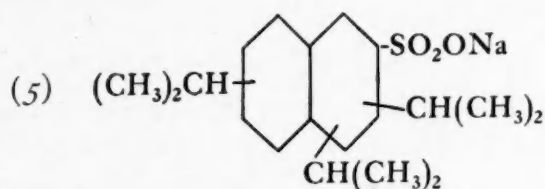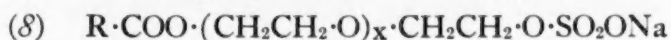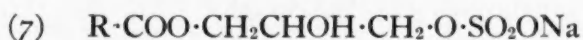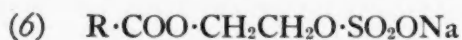
The alkyl esters of 4-sulfophthalic acid also belong to this class.

About 1928 the esters and amides of sulfonated fatty acids appeared, based on the theory that the carboxyl group was the cause of hard-water instability. They are better wetting agents than sulfonated oils, but are poor detergents.

As a result of an economical method for the reduction of fatty acids to fatty alcohols, the sulfuric esters of the latter were produced commercially in 1929. These esters are good detergents, and also possess the desirable properties of the sulfonated oils. They were immediately employed as assistants in dyeing and textile processing. As commercially supplied, these compounds are usually the sulfates of mixtures of alcohols that are obtained from available fatty ma-

terials. While the sodium salts are more widely known, amine salts are used for special purposes, such as shampoos. Sodium alkyl sulfates show maximum wetting action at C_{12} (sodium lauryl sulfate) and maximum detergent activity at C_{18} (sodium stearyl sulfate).

Other sulfates having excellent detergent properties and stability in hard water are prepared from fatty acid esters, thus avoiding the use of the somewhat more expensive fatty alcohols. Examples of general groups are—

(6) $R \cdot COO \cdot CH_2CH_2O \cdot SO_2ONa$

(7) $R \cdot COO \cdot CH_2CHOH \cdot CH_2 \cdot O \cdot SO_2ONa$

(8) $R \cdot COO \cdot (CH_2CH_2 \cdot O)_x \cdot CH_2CH_2 \cdot O \cdot SO_2ONa$

Such esters are, of course, not stable to acids and alkalies.

Sodium oleyl methyl taurine (9) is resistant to hydrolysis and is an efficient detergent, even in an acid solution.

(9) $CH_3(CH_2)_7 \cdot CH = CH(CH_2)_7 \cdot CO \cdot N(CH_3) -$
$CH_2CH_2SO_2ONa$
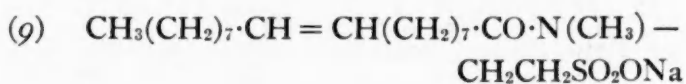
Another class of excellent detergent and wetting agents is made by sulfonating alkyl benzenes that are prepared from kerosene monochlorides and benzene by aluminum chloride catalysis. In the general structure (10), R is a mixture approximated by $C_{12}H_{25}$ to $C_{18}H_{37}$.
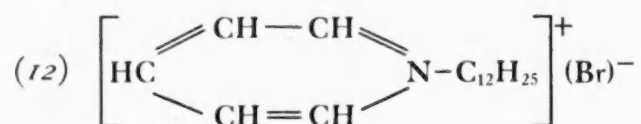
(10) R SO_2ONa

While sulfonates and sulfates are very important, reagents utilizing alkali-metal carboxylates as polar groups are also useful. Naphthenic acid soaps have recently become available in purified form, and have somewhat intermediate properties between those of the common soaps and the sulfonated materials. Other carboxyl types are made from other waste proteins, such as leather scrap, by hydrolysis with alkali followed by reaction with oleyl chloride, or a similar compound. Synthetic materials having similar properties may be typified by the formula—

(11) $C_{18}H_{34}CO \cdot NH \cdot (CH_2CONH)_x \cdot CH_2 \cdot COONa$

Previous to the development of the surface-active compounds that have been described, the bile acids were known to be useful for certain purposes, particularly for washing silk. Such purified products of bile extract as sodium choleate, sodium taurocholate, and sodium glycocholeate have properties that make them suitable for small-scale specialized applications.

An interesting departure from established practice involves the "reversed" soaps, or cation-active compounds, that are exemplified by the alkyl pyridinium salts, such as lauryl pyridinium bromide which has the structure—

$$(12) \quad \left[HC \begin{array}{c} {}^{\nearrow}CH - CH_{\searrow} \\ \\ {}_{\searrow}CH = CH^{\nearrow} \end{array} N - C_{12}H_{25} \right]^{+} (Br)^{-}$$

Uses for this and other surface-active, quaternary-nitrogen compounds include wetting in acid liquids—for carbonizing, hat making, dyeing, and chrome tanning; and the washing of lime salts from wool, in the presence of hydrochloric acid. Cation-active compounds are substantive on cotton and, hence, useful for mordanting and for after-treatment to improve fastness of dyes.

Internally neutralized surface-active compounds, such as the betaines, have been described in the patent literature. The R group in the general structure (13) may be an aliphatic chain containing from 8–18 carbon atoms.

$$(13) \quad \begin{array}{c} CH_3 \\ | \\ R - N^{+} - CH_2COO^{-} \\ | \\ CH_3 \end{array}$$
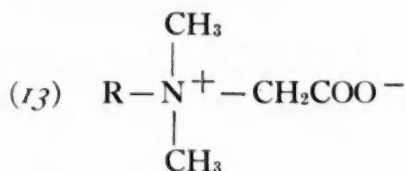
Nonionic surface-active compounds have the advantage of not being affected by the pH of the solutions in which they are used; and they are, of course, stable in hard water. Examples are the monostearyl, lauryl, and oleyl ethers of polyethylene glycol, which have the following general structure—

$$(14) \quad R \cdot O \cdot (CH_2CH_2O)_x \cdot CH_2CH_2OH.$$

Eastman Organic Chemicals, List No. 32
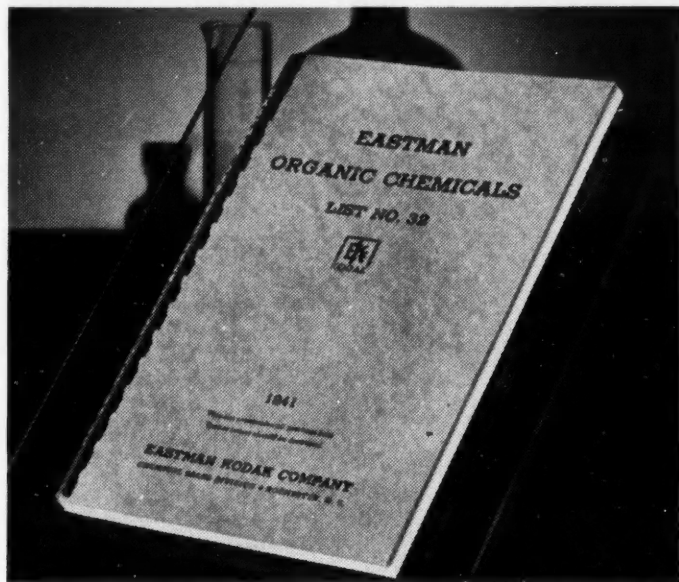
A PRIMARY PURPOSE of the Eastman Kodak Company in establishing a source of organic chemicals was to increase the number of compounds offered as rapidly as new ones could be prepared in the Kodak Research Laboratories, or became available. The new catalog, *Eastman Organic Chemicals, List No. 32,* is tangible proof of how well this policy has been carried out. Included in the list are 166 compounds that have not previously appeared therein, making a total of nearly 3,500 different chemicals. Price changes were, of course, necessary in a number of instances; but in most cases they were reductions made possible by larger production and improved methods. A few items were increased in price because of higher costs of raw materials.

Those who are interested in specific groups of chemicals will appreciate the new sections at the back of the catalog. Collected there for easy reference are lists of compounds available in these classes: vitamins and related products; sugars; amino acids; carcinogenic hydrocarbons; alkaloids; and liquids for refractive index determinations. The lists of special reagents, indicators, and special "spot test" reagents are retained.

Eastman Organic Chemicals, List No. 32, became effective May 1, 1941. If you have not as yet received your copy, one will be forwarded free upon request.

Karl Fischer Reagent for the Determination of Water

THIS REAGENT, as originally described by Karl Fischer (*1*), was a solution of iodine, sulfur dioxide, and pyridine, in methanol. While the chemical reactions that take place in its use for the determination of water are complex (*2*), the method is specific if the conditions are carefully controlled. The end point of the reaction may be detected colorimetrically, by adding the Karl Fischer reagent to a solution containing water until its chromate-yellow color changes to brown; or electrometrically, by adding an excess of the reagent to the solution and back-titrating with a standard solution of water in methanol (*3*).

The Karl Fischer reagent is satisfactory for determining water in both organic and inorganic liquids and solids. Alcohols, hydrocarbons, esters, and carboxylic acids, with the exception of formic acid, do not interfere.

Water cannot be determined satisfactorily in aldehydes and ketones by the use of the reagent as it was originally described. However, if the methanol content is greatly reduced and the amount of pyridine increased, a modified form is obtained that reacts normally when in solution with ketones, provided large quantities of the lower alcohols are not present (*4*). Interference of carbonyl compounds may be precluded by the use of pyridine solutions of hydrogen cyanide (*5*), since the cyanhydrins that are formed are inert toward the reagent.

The possibility of adapting the Karl Fischer reagent to analytical procedures that involve chemical reactions in which water is either eliminated or absorbed makes it especially useful. For example, alcoholic hydroxyl can be determined by esterification with glacial acetic acid, in the presence of boron trifluoride—the water thus formed being titrated with the reagent (*6*). Aliphatic acids, including branched-chain and hydroxyl-substituted types, and aromatic acids having the carboxyl group attached to an aliphatic side chain can be esterified with methanol, using boron trifluoride as a catalyst—the liberated water being titrated with the reagent (*7*).

Analysis of acid anhydrides may be carried out by adding a known amount of water, the quantity being more than that required for complete hydrolysis of the anhydride, and then titrating the excess water with the Karl Fischer reagent (*8*). Carbonyl compounds may be determined by treatment with hydroxylamine hydrochloride, stabilization of the amine with ethyl acetate, and titration of the liberated water (*9*).

In the preparation of the Karl Fischer reagent, particularly the modified form, purity of the ingredients and the absence of water are especially important. If care is taken in these respects, less iodine will be required, fewer colored by-products will be present to obscure the visual end point, and deposition of objectionable material on glassware will be precluded. In order to meet the requirements of purity, a special grade of pyridine has been added to the stock of Eastman chemicals, as *Eastman 214-H Pyridine (for Karl Fischer Reagent)*.

Literature Cited

(*1*) Fischer, *Angew. Chem.*, 48, 394 (1935).

(*2*) Smith, Bryant, and Mitchell, *J. Am. Chem. Soc.*, 61, 2407 (1939).

(*3*) Almy, Griffen, and Wilcox, *Ind. Eng. Chem., Anal. Ed.*, 12, 392 (1940).

(*4*) Smith, Bryant, and Mitchell, *J. Am. Chem. Soc.*, 61, 2409 (1939).

(*5*) Bryant, Mitchell, and Smith, *J. Am. Chem. Soc.*, 62, 3504 (1940).

(*6*) Smith, Bryant, and Mitchell, *J. Am. Chem. Soc.*, 62, 1 (1940).

(*7*) Mitchell, Smith, and Bryant, *J. Am. Chem. Soc.*, 62, 4 (1940).

(*8*) Smith, Bryant, and Mitchell, *J. Am. Chem. Soc.*, 62, 608 (1940).

(*9*) Mitchell, Smith, and Bryant, *J. Am. Chem. Soc.*, 63, 573 (1941).